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CLINKER BRICK BASED ON CRUDE KAOLIN AND SLUDGES FROM ALKALI ETCHING

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It is shown that sludges due to alkali etching and used as a grog additive in ceramic mixes based on crude kaolin clay make it possible to obtain clinker articles of high quality.

Key words: clinker articles, crude kaolin, sludges from alkali etching, chemical composition, glass phase, crystals, mullite, hematite, quartz.

Clinker ceramics are artificial stony materials with a set shape which are formed from clay by firing in the temperature range 1250 – 1350°C to complete sintering without vitrification of the surface. These materials are stone commodity with rough pieces. Clinker ceramic materials are distinguished from ordinary articles of coarse construction ceramics (ordinary brick, tiles, facing tiles) by higher mechanical strength (compressive, durability, bending) and lower water absorption (0 – 6 wt.%). Such high indicators are due to the structure and phase composition of the materials. Clinker ceramic materials contain large amounts of a glass phase. The structure of clinker ceramic materials is dense, micrograin-size, with no large inclusions, voids, and flaws. It is precisely such a structure that gives such high performance.

The objective of the present work is to obtain clinker brick based on crude kaolin and sludges from alkali etching.

Crude kaolin from the Chapaevskoe deposit in Samara Oblast was used as a clay component to produce clinker ceramic articles [1]. The following oxides represent the chemical composition of crude kaolin, %:[3] 65 – 75 SiO_2; 10 – 18 Al_2O_3; 1 – 3.5 Fe_2O_3; 2 – 3.5 CaO; 0.5 – 2 MgO; R_2O (R_2O = Na_2O + K_2O) — 0.1 – 0.5; other — 4 – 6. The low aluminum oxide content (10 – 18 Al_2O_3) of crude kaolin makes it impossible to obtain from it acid- and heat-resistant clinker ceramic articles. On the basis of the content of 0.001 mm particles (30 – 35%) the clay is a coarsely disperse raw material, it is definitely plastic (plasticity number 10 – 12), and it is refractory (fire-resistance 1530 – 1550°C).

Sludges obtained from alkali etching are metallurgical and metal-processing wastes [2]. They are formed in metallurgical plants when concentrated solutions are used to process aluminum alloys. As a rule, such alloys consist of sodium hydroxide with a small amount of special substances. The following oxides represent the chemical composition of the sludges, %: 0.3 – 0.8 SiO_2; 43 – 57 Al_2O_3; 1.5 – 6.8 Fe_2O_3; 0.5 – 9 CaO; 0.5 – 4 MgO; 6 – 12 R_2O; 0.5 – 6 SO_3.

Distinguishing features of all sludges are high values of the following:

dispersity — 8000 – 10,000 cm^2/g;

plasticity (plasticity number > 10), which makes it possible to use low-plasticity crude kaolins for the production ceramic clinker articles.

The high content of aluminum oxide (43 – 57% Al_2O_3) in sludge makes it possible to increase the acid-resistance, heat-resistance, and mechanical strength under bending of clinker articles.

The ceramic mix was prepared by a plastic method with moisture content 18 – 22% and from which 250 × 120 × 65 mm bricks were made. The dried bricks (residual moisture not exceeding 5%) were fired at 1000°C (appearance of a liquid phase) and 1300°C (final firing temperature). Table 1 shows the compositions of the ceramic mixes and Table 2 the

TABLE 1. Compositions of Ceramic Mixes

Component	Component content, wt.%			
	1	2	3	4
Crude kaolin	70	60	50	40
Sludges from alkali-etching of aluminum	30	40	50	60

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[3] Here and below — content by weight.

TABLE 2. Physical-Mechanical Brick

Indicator	Composition			
	1	2	3	4
Maximum strength under bending, MPa	70	72	78	82
Frost resistance, cycles	160	165	174	181
Shrinkage, %	8.8	9.3	10.2	10.8
Heat-resistance, thermal cycling	17	18	18	19
Acid-resistance, %	98.7	98.9	99.2	99.3

physical-mechanical and chemical properties of the clinker bricks at the final firing temperature.

As Table 2 shows, the clinker ceramic articles made from the proposed compositions have high strength, frost resistance, heat resistance, and acid resistance.

The use of production wastes in obtaining clinker articles makes possible salvaging industrial wastes, environmental protection, and expansion of the raw materials resource base for the production of ceramic materials.

In the development of silicate materials, special attention is focused on the investigation of the microstructure, since the microstructure and phase composition mainly determine the functional properties of ceramic articles [3].

In studying a ceramic clinker article in an electron-microscope great difficulties are encountered in obtaining replicas from the samples, especially samples which are fired in the temperature range 1000 – 1050°C, when the liquid phase contains many undissolved clayey particles [3].

In samples fired at 1000°C, colorless yellowish and brownish glasses with refractive indices from 1.50 to 1.54, forming as a result of melting of spars (Fig. 1), are visible under a microscope. The appearance of a liquid phase in the experimental samples is likewise explained by a high content of alkali (6 – 12% R_2O) in the sludges from alkali etching.

Ceramic brick sinters with the participation of a liquid phase, on whose properties the process resulting in the formation of the structure and properties of the material largely depends. Increasing the reactivity of the liquid phase in ceramic brick with respect to refractory components makes it possible to intensify the sintering process, which will make it possible to decrease fuel consumption [3 – 4].

Increasing in ceramic mixes the content of sludges from alkali etching to 60% (see Table 1) will make it possible to increase the content of the glass phase in brick (See Fig. 1*d*). The refractive indices increase from 1.50 (compositions 1 – 2, see Fig. 1*a* and *b*) to 1.54 (compositions 3 – 4, see Fig. 1*c* and *d*). This could be due to a transition of, aside from R_2O, some fraction of Fe_2O_3 into glass [4].

B. I. Vinogradov indicates in [5] that melt initially appears at the boundary of particles of difference chemical composition as a result of the formation of low-melting eutectics, which are based on K_2O, Na_2O, and FeO.

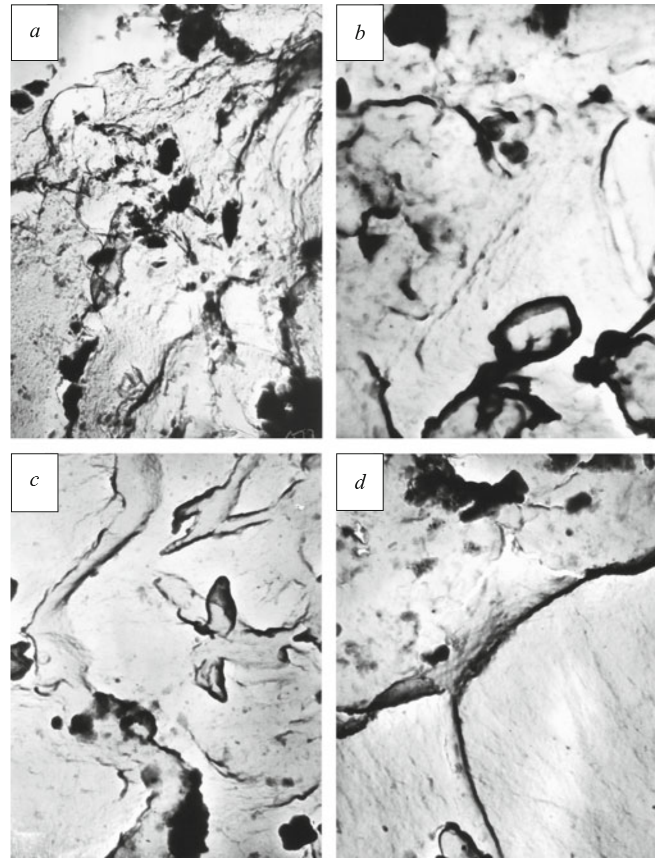

Fig. 1. Microstructure of samples with different composition (× 5000) *a*) 1; *b*) 2; *c*) 3; *d*) 4.

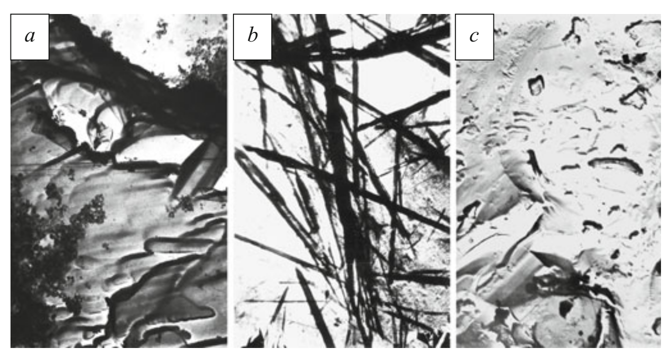

Fig. 2. Microstructure of ceramic clinker material (composition 4; × 15000): *a*) glass-phase field; *b*) mullite crystals with a needle habit; *c*) hematite crystals with pellet and pellet-pyramidal habit; *d*) melted quartz crystals with a prismatic habitus.

Increasing the firing temperature to 1300°C results in the formation of mullite, which imparts the main physical-mechanical and chemical properties to clinker brick.

Electron-microscopic studies showed a glass-phase field (Fig. 2*a*), substantial accumulations of spinel crystals, large mullite crystals with a needle habit (Fig. 2*b*), clusters of contoured hematite crystals with pellet and pellet-pyramidal habits, and melted crystals of quartz with a prismatic habitus (Fig. 2*c*).

Colorless, yellowish, and brown glasses with index of refraction from 1.55 to 1.59 are observed in samples under a microscope. These glasses were formed as a result of melting of spars and mixed-layered clayey formations.

An elevated content of iron oxide (1.5 – 6.8% Fe_2O_3) and alkali (6 – 14% R_2O) in sludges from alkali etching gives rise to the appearance of a substantial quantity of a liquid phase at 1300°C.

In summary, the present investigations have shown that the use of sludges from alkali etching as grog in ceramic mixes based on crude kaolin clay makes it possible to obtain clinker articles of high quality.

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